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EVALUATION OF EUTECTIC FLUORIDE THERMAL ENERGY STORAGE UNIT COM--ETC(U)
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AFAPL-TR-75-92
PART II

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EVALUATION OF EUTECTIC FLUORIDE THERMAL ENERGY STORAGE UNIT COMPATIBILITY

PART II - TEST PROCEDURES AND POST-TEST EVALUATION RESULTS

AEROSPACE POWER DIVISION
ENERGY CONVERSION BRANCH

MARCH 1977

TECHNICAL REPORT AFAPL-TR-75-92, PART II

INTERIM REPORT FOR OCTOBER 1975 TO JUNE 1976

Approved for public release; distribution unlimited

AIR FORCE AERO-PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This report contains the results of an effort to evaluate the stability and the corrosion rates of fluoride eutectic thermal energy storage salts. The work was performed in the Energy Conversion Branch of the Air Force Aero-Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson AFB, Ohio under Project 3145, Task 19 and Work Unit 49. The effort was conducted by Jerry Beam during the period October 1975 to June 1976.

This technical report has been reviewed and is approved for publication.

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The objective of this work is to develop the required analytical and experimental heat transfer and metallurgical compatibility data necessary to optimize the design and usable life of thermal energy storage systems for surveillance spacecraft VM cryocooler applications. This report will discuss the initial 2000 hours of metallurgical data and the techniques used to obtain this data for various eutectic fluoride thermal energy storage systems.

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AFAPL-TR-75-92
Part II

FOREWORD

This report contains the results of an effort to evaluate the stability and the corrosion rates of fluoride eutectic thermal energy storage salts. The work was performed in the Energy Conversion Branch of the Air Force Aero-Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson AFB, Ohio under Project 3145, Task 19 and Work Unit 49. The effort was conducted by Jerry Beam during the period October 1975 to June 1976.

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INTRODUCTION

The use of Thermal Energy Storage for I.R. surveillance satellite Vuilleumier (VM) cryocooler application is currently being studied by AFAPL as an alternative to electrochemical energy storage for providing eclipse power of 1 KW-HR at 1000-1250°F to the VM cryocooler. The AFAPL is presently sponsoring and conducting research on the system design and materials selection for this concept. In order to design flight weight, long life hardware, corrosion rate data and eutectic salt, temperature stability needs to be determined. To accomplish this, two experiments were devised and are described here. Post 2000-hour test sample metallurgical evaluations are also described.

1. DIRECTLY HEATED CLAD TEST

The purpose of this test is to determine the stability of the transformation temperature and the feasibility of using the containment material as the heater. Capsules were fabricated and filled with an eutectic salt and copper blocks attached to the capsule for electrical connections. This eliminated the need for a separate heater to melt the salt. The capsules were then instrumented with chromel-alumel (type K) thermocouples along the top and bottom lengths of the capsule. To minimize the heat losses, two layers of high temperature flexible insulation and two layers of 3-mil stainless steel were wrapped in concentric, alternate layers around the capsule, thermocouples, and copper connectors, and secured with Inconel wires. The insulated capsule was then loaded in a vacuum chamber and connected to a multichannel temperature recording unit and a 300-ampere power supply.

To conduct the test, electrical current was passed through the container clad and the I^2R heating of the clad was used to heat the salt. During heat up and cool down, thermocouple data was recorded and compiled to determine the stability of the transition temperature. At the end of the test, the capsules were cut apart and evaluated.

2. TIME-AT-TEMPERATURE EXPERIMENT

The purpose of this experiment is to determine the amount of clad material needed to contain the molten salts. Thinner wall thicknesses mean lighter flight hardware and also ease the interface problem for a directly heated clad system to the spacecraft power bus. For this experiment, three capsules of an eutectic salt were fabricated and held at a temperature at or about the eutectic temperature of the salt. At intervals of 3, 6, and 12 months, a capsule will be removed and cut apart to determine the corrosion rate data.

In the test set up by AFAPL, a total of nine capsules were fabricated (three different eutectics salts). Each of the capsules were instrumen[illegible]ith a chromel-alumel thermocouple and connected to a multi-channel [illegible]or.

To supply the heat, a vacuum, temperature controlled, furnace was used. The temperature profile of the furnace was measured for different power settings and the final setting selected such that each capsule could be positioned in the oven at a temperature at or about the needed transition temperature. The capsules were then positioned in the oven, vacuum applied, and heated to their transition temperatures.

SECTION II

CAPSULE DESCRIPTION

The capsules for these two experiments were fabricated by the University of Dayton Research Institute (UDRI) and the complete fabrication process is covered in AFAPL-TR-75-92, Part I, "Evaluation of Eutectic Fluoride Thermal Energy Storage Unit Compatibility." Briefly, all capsules were fabricated from Inconel 617 with Inconel end caps E-beam vacuum welded. The eutectic fluoride compositions used to fill the capsules are listed in Table 1.

TABLE 1

TEST MATRIX FOR EUTECTIC FLUORIDE COMPATIBILITY TEST

Capsule No.	Eutectic Material	Eutectic Temp (°C)	Test
1	$LiF-MgF_2$	725	T@T
2	$LiF-MgF_2$	725	T@T
3	$LiF-MgF_2$	725	T@T
4	$LiF-MgF_2-NaF$	686	T@T
5	$LiF-MgF_2-NaF$	686	T@T
6	$LiF-MgF_2-NaF$	686	T@T
7	$LiF-MgF_2-KF$	705	T@T
8	$LiF-MgF_2-KF$	705	T@T
9	$LiF-MgF_2-KF$	705	T@T
10	$LiF-MgF_2-NaF$	686	DHC
11	$LiF-MgF_2-KF$	705	DHC

Notes:

1. The Time-at-Temperature (T@T) capsules are 1" O.D. x 3" long.
2. The Directly Heated Clad (DHC) capsules are 1" O.D. x 12" long.
3. All clad thicknesses are 64 mils.

SECTION III

TEST RESULTS

1. DIRECTLY HEATED CLAD RESULTS

The directly heated clad experiment was conducted with two different approaches. The first 1000 hours of tests were conducted with a constant current flow through the clad. To melt the salt, 250 amps of D.C. current were passed through the clad. The temperature profile was monitored and when evidence of a melt occurred, as indicated in Figure 1, the current was reduced to 200-225 amps and held there for up to three hours. After the idle period, the current was reduced to 150 amps and left for the next day's cycle.

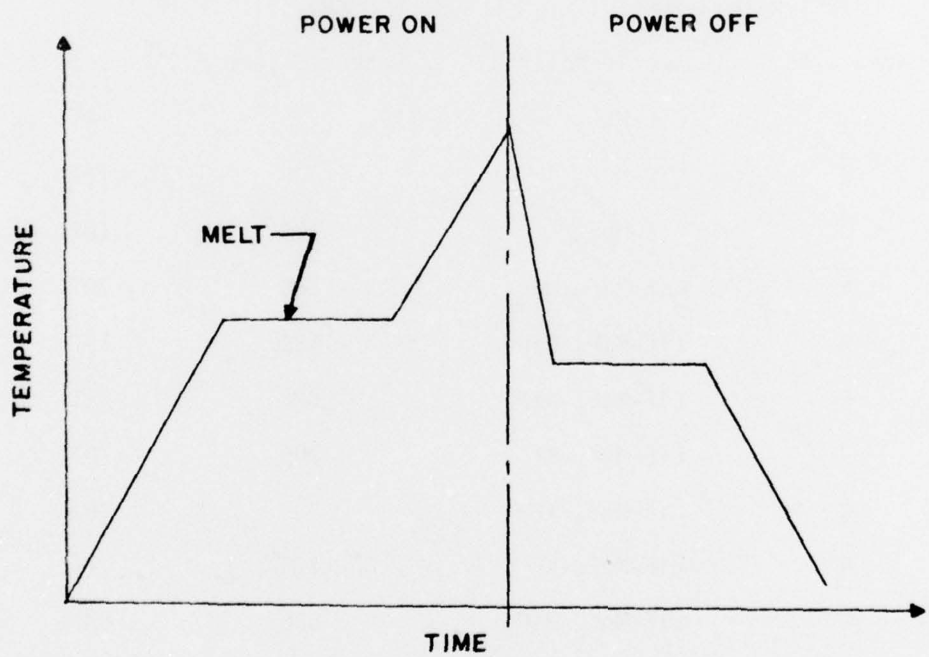

Figure 1. Typical Cycle Curve

This cycling was conducted 40 times with no apparent degradation of the material. Figures 2 and 3 show the typical temperature profiles of the capsule. No degradation of the eutectic composition is evident. At the end of this cycling (better than 1000 hours of testing) the chamber

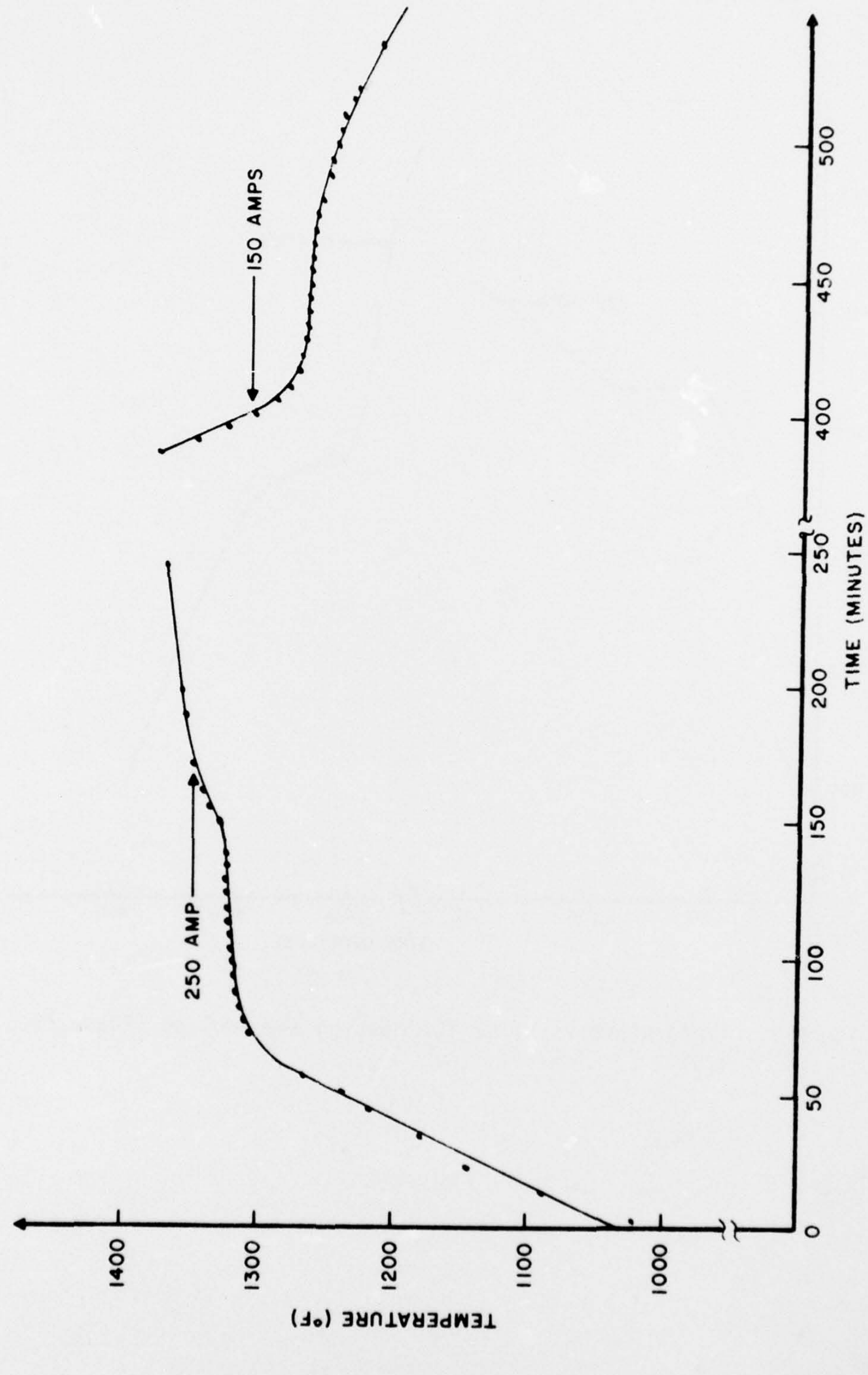

Figure 2. Temperature vs. Time for Heating and Cooling (Phase I)
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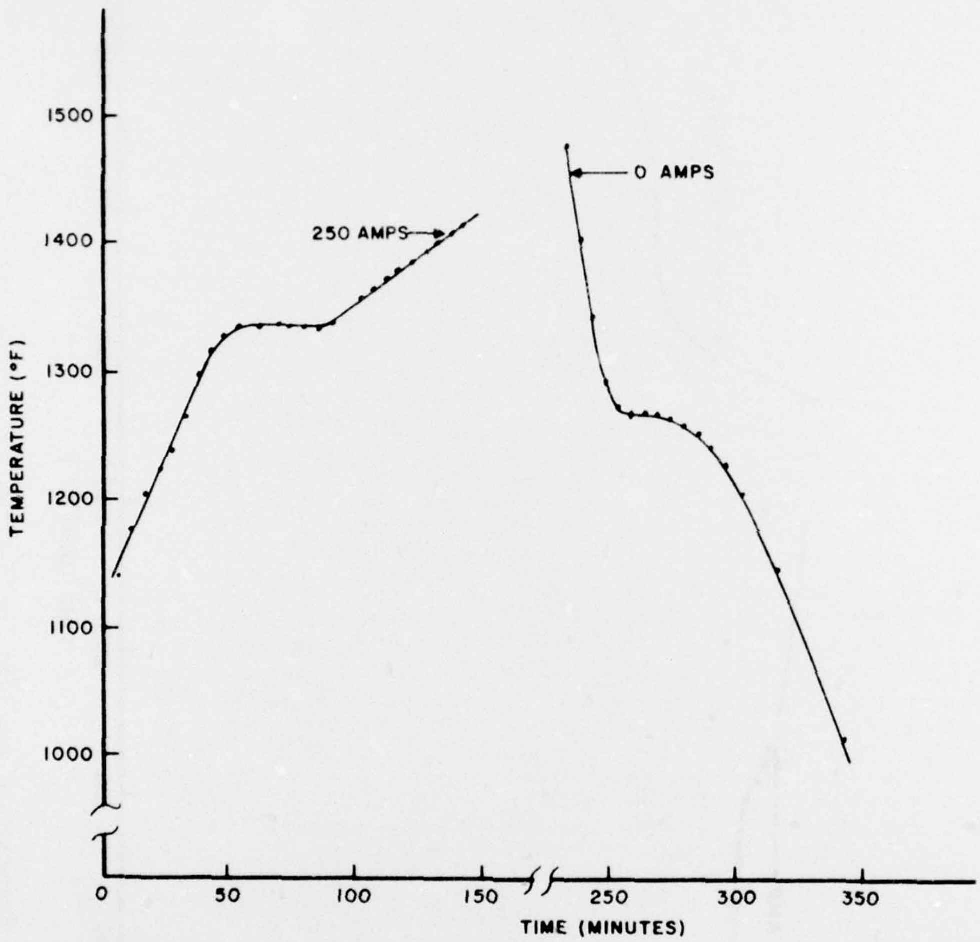

Figure 3. Temperature vs. Time for Heating and Cooling (Phase I)
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was opened and the capsule unwrapped for evaluation. Visual examination of the capsule indicated some copper diffusion into the Inconel clad from the power connector. The diffusion bond was weak and the two were separated by hand. With no other apparent defects, the capsule was subjected to radiographs and a die penetrant test. Both tests indicated no defects in the clad material.

Then the capsule was re-instrumented with thermocouples and insulated as before and put back on test. The test procedure for this phase of the test was modified to allow continuous, unattended cycling of the device. To allow continuous cycling, several of the thermocouples were connected to relay circuits to cycle the power supply automatically. The power supply remained on until the salt content had melted completely and was allowed to raise 55°C (100°F) above the melt temperature. At this time, the power supply was automatically shut off and the capsule allowed to cool below the melt temperature. This new set up allowed continuous operation and acquired data on up to 12 complete cycles per day.

The test was continued for 500 cycles at which time the capsule was again removed for evaluation; approximately 2000 hours at elevated temperature had been accumulated. No visual defects were evident, and the capsule was cut apart in radial sections for examination. The only visible defect was a very minute amount of pitting on the clad walls. The capsules were then packaged, and sent to UDRI for post-test evaluation.

2. POST EVALUATION BY UDRI

This material was characterized through a combination of tests that included Differential Thermal Analysis (DTA), and X-ray diffraction analysis. These tests are fully explained in AFAPL-TR-75-92, Part I, "Evaluation of Eutectic Fluoride Thermal Energy Storage Unit Compatibility". The 12-inch capsule from this experiment was sectioned into seven segments with one sample selected from each end and the other five at two-inch increments along the length of the sample. The DTA test on these samples resulted in one extra thermal event on two of the seven samples. This extra event occurred on the end of the capsule in which the instrument leads and the power leads were fed through the insulation bundle. This cooled the one

end faster than the other and it is speculated that this resulted in a precipitation-solution reaction at this cooler end. (The pro-eutectic constituents will precipitate from the liquid phase prior to the solidification of the eutectic composition.) The observed temperatures of the temperature events are listed in Table 2.

TABLE 2

DTA TEST RESULTS OF DHC SAMPLE ($LiF-MgF_2-NaF$)

Sample No.	Temp. (°C)	Event	Cycle
1 (cool end)	657	(solvus)	Heating
	688	eutectic	Heating
	728-732	liquidus	Cooling
	684	eutectic	Cooling
	650	(solvus)	Cooling
2	657	(solvus)	Heating
	688	eutectic	Heating
	713-722	liquidus	Cooling
	686	eutectic	Cooling
	654	(solvus)	Cooling
3	657	(solvus)	Heating
	684	eutectic	Heating
	686	eutectic	Cooling
	653	(solvus)	Cooling
4	659	(solvus)	Heating
	686	eutectic	Heating
	686	eutectic	Cooling
	655	(solvus)	Cooling

TABLE 2 (CONTINUED)

Sample No.	Temp. (°C)	Event	Cycle
5	660	(solvus)	Heating
	685	eutectic	Heating
	688	eutectic	Cooling
	654	(solvus)	Cooling
6	659	(solvus)	Heating
	688	eutectic	Heating
	688	eutectic	Cooling
	654	(solvus)	Cooling
7	654	(solvus)	Heating
	693	eutectic	Heating
	693	eutectic	Cooling
	650	(solvus)	Cooling

The major event in every sample was the eutectic transformation which occurred at a temperature of 688$\pm$5°C. The minor transformation was observed in the range of 650° to 660°C and is attributed to the precipitation-solution reaction in the solid state as the solvus boundary is crossed.

The X-ray diffraction analysis on this capsule resulted in diffraction peaks that are in a one-to-one correspondence with the pre-exposure test. In conclusion, the test conducted on this sample indicated that the salt, in its liquid state, could be contained in the Inconel 617 alloy without any significant change in its transformation temperature.

3. RESULTS OF THE TIME-AT-TEMPERATURE TEST

One capsule of each type eutectic was removed from the furnace. After 2000 hours of testing, no visual defects were present and the capsules were sent to UDRI for post test analysis. The UDRI subjected each of these capsules to the following three tests: (1) Differential Thermal Analysis (DTA) to determine the transition temperature; (2) X-ray diffraction analysis to determine the crystal structure of the salts; and (3) Scanning electron microprobe analysis to determine the location of the chemical components of the eutectic. The results of these tests are as follows.

a. LiF-MgF_2 Results

Two different areas were identified within the material, one with a darkened appearance while the other remained as the pre-tested salt. Two individual DTA's were conducted in each of these areas. The results of this test are tabulated in Table 3.

TABLE 3

TEST RESULTS FOR DTA ON LiF-MgF_2

Sample	Temp. °C	Event	Cycle
Pre-Test	725	Eutectic	Heating
	735	Liquidus	Cooling
	722	Eutectic	Cooling
Post-Test 1 Dark Salt	649-662		Heating
	726	Eutectic	Heating
	654-659		Cooling
	722		Cooling
	742		Cooling

TABLE 3 (CONTINUED)

Sample	Temp. °C	Event	Cycle
Post-Test 2 Dark Salt	649-662		Heating
	726	Eutectic	Heating
	653-657		Cooling
	723	Eutectic	Cooling
	739	Liquidus	Cooling
Post-Test 1	664		Heating
Clean White Salt	727	Eutectic	Heating
	655-659		Cooling
	722	Eutectic	Cooling
	742	Liquidus	Cooling
Post-Test 2	659-664		Heating
Clean White Salt	727	Eutectic	Heating
	653-657		Cooling
	722	Eutectic	Cooling
	742	Liquidus	Cooling

The results indicate that eutectic temperatures have remained stable. The increase in the liquidus transition temperature indicates that the composition is slightly off of the eutectic composition and the 653° to 659°C event is probably a solid state precipitation phase. The X-ray analysis for both of these samples are the same for the pre- and the post-evaluation and the microprobe result confirm the DTA and X-ray analysis. From these results, it is concluded that the two areas of the salt are only different in crystal structure and do not represent a contamination of the salt.

b. $LiF-MgF_2$ - NaF Results

No degradation of this crystal composition was visually indicated. The two DTA results are listed in Table 4.

TABLE 4

TEST RESULTS FOR DTA ON $LiF-MgF_2-NaF$

Sample	Temp °C	Event	Cycle
Pre-Test	686	Eutectic	Heating
	703	Liquidus	Cooling
	687	Eutectic	Cooling
Post-Test 1	620	Eutectic	Heating
	620	Liquidus	Cooling
	616	Eutectic	Cooling
Post-Test 2	620	Eutectic	Heating
	622	Liquidus	Cooling
	616	Eutectic	Cooling

There is a definite change in this particular eutectic temperature. X-ray analysis also indicates a change in constituents present in the post-test sample. Pre-test samples indicated the presence of LiF, MgF_2, and $MgF_2 \cdot NaF$ while post-test samples show LiF, NaF, and $MgF_2 \cdot NaF$. The microprobe also confirms the presence of NaF in the microstructure. Further testing conducted to analyze this change in eutectic temperature and composition indicated that the salts fabricated for this test were mixed at the wrong eutectic compositions. Replacement capsules have since been fabricated and are now on test.

c. $LiF-MgF_2-KF$ Test Results

Again, no visual defects were observed in the salts. The two DTA results are tabulated in Table 5.

TABLE 5

TEST RESULTS FOR DTA ON LiF-MgF_2-KF

Sample	Temp °C	Event	Cycle
Pre-Test	750	Eutectic	Heating
	710	Liquidus	Cooling
	701	Eutectic	Cooling
Post-Test 1	648-655		Heating
	708	Eutectic	Heating
	645-647		Cooling
	713	Liquidus	Cooling
	703	Eutectic	Cooling
Post-Test 2	648-655		Heating
	710	Eutectic	Heating
	645-647		Cooling
	712	Liquidus	Cooling
	703	Eutectic	Cooling

These results indicate no significant change in the eutectic temperatures. The new event from 645° to 655°C observed here is again probably related to a solid state precipitation phase. The X-ray analysis of the post-test sample shows the same results as the pre-test samples and the microprobe analysis confirms the DTA and X-ray analysis.

SECTION IV

CONCLUSIONS

1. No significant amount of corrosion of the clad materials has resulted from the first 2000 hours of testing. Therefore, the next set of capsules will not be evaluated for another year (10,000 hours).

2. The eutectic temperatures have remained stable.

3. The initial test has proven successful from a compatibility standpoint and follow-on work is to be conducted to improve and verify the application for VM coolers.

SECTION V

WORK TO BE CONDUCTED

1. Capsule 12, directly heated clad sample, will continue to be tested by Arizona State University. At end of life, the capsule will be returned to AFAPL for evaluation.

2. The time-at-temperature capsules will continue to be held at temperature. Since the 2000-hour results showed such an insignificant amount of corrosion, the second set of capsules will not be removed until 10,000 hours of testing have been accomplished.

3. An oxide program has just been initiated to study the possibilities of substituting oxide eutectic compositions for the current fluorides. Materials are to be investigated for their thermal conductivity, density, heat of fusion, and volume expansion. Candidate materials will then be fabricated in capsules and sent to AFAPL for life testing.

4. Six new directly heated clad samples have been obtained. The wall thickness of the new capsules is only 32 mils which will ease the heating problem. These capsules will be connected in series and life tested from a systems approach.

5. A demonstration is being planned to couple a TES unit to a VM cryocooler. The VM cryocooler is presently on test with an electrically heated hot cylinder and plans are to remove the hot cylinder and replace it with a specially designed heat pipe-TES integral cylinder.

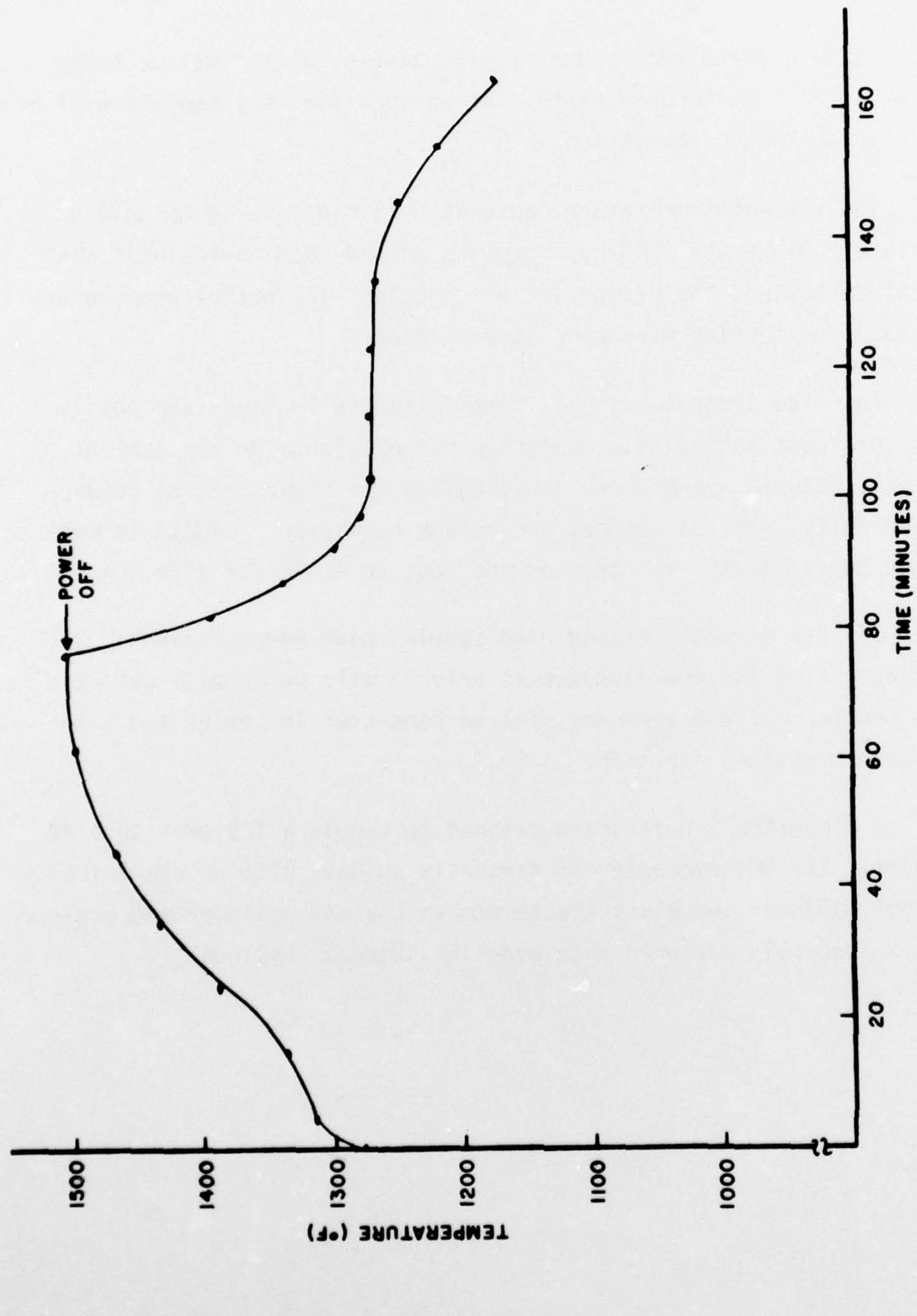

Figure 4. Temperature vs. Time for Heating and Cooling (Phase II)
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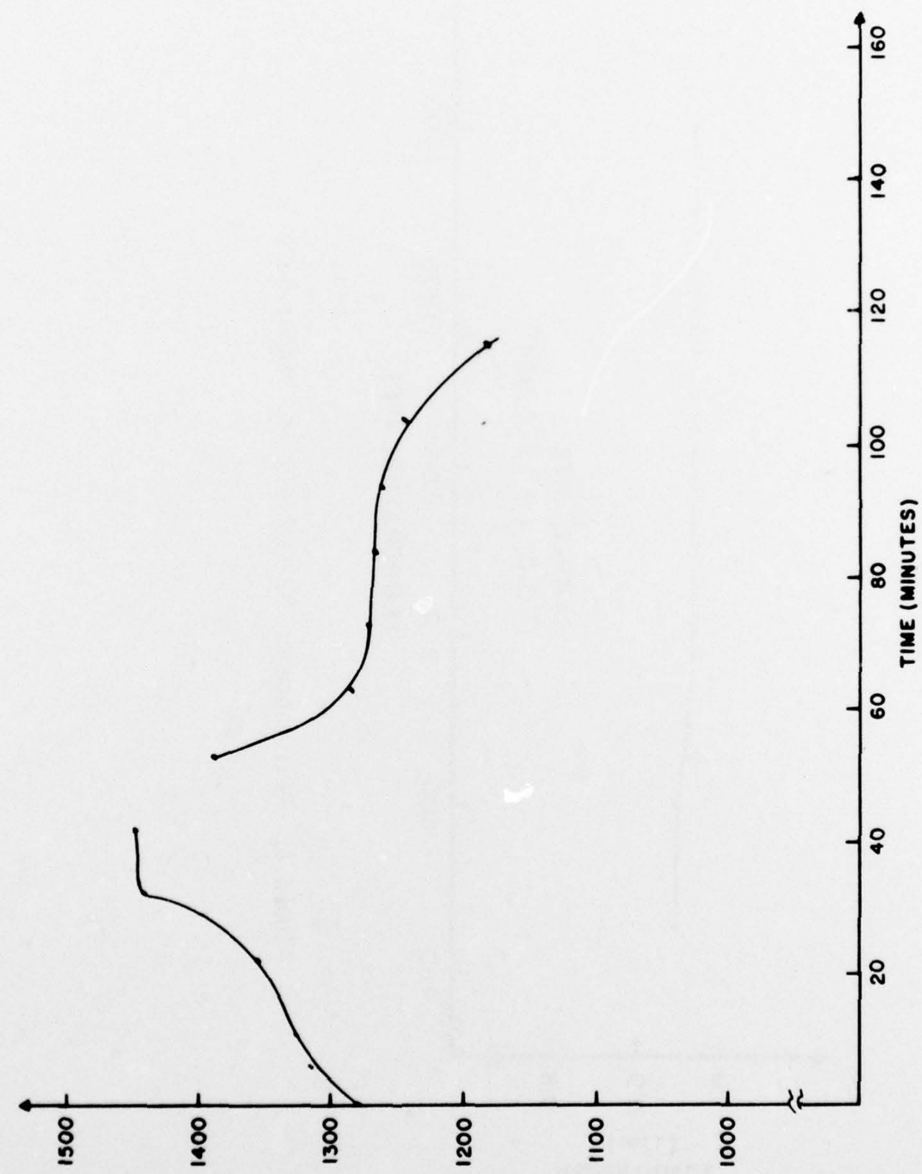

Figure 5. Temperature vs. Time for Heating and Cooling (Phase II)
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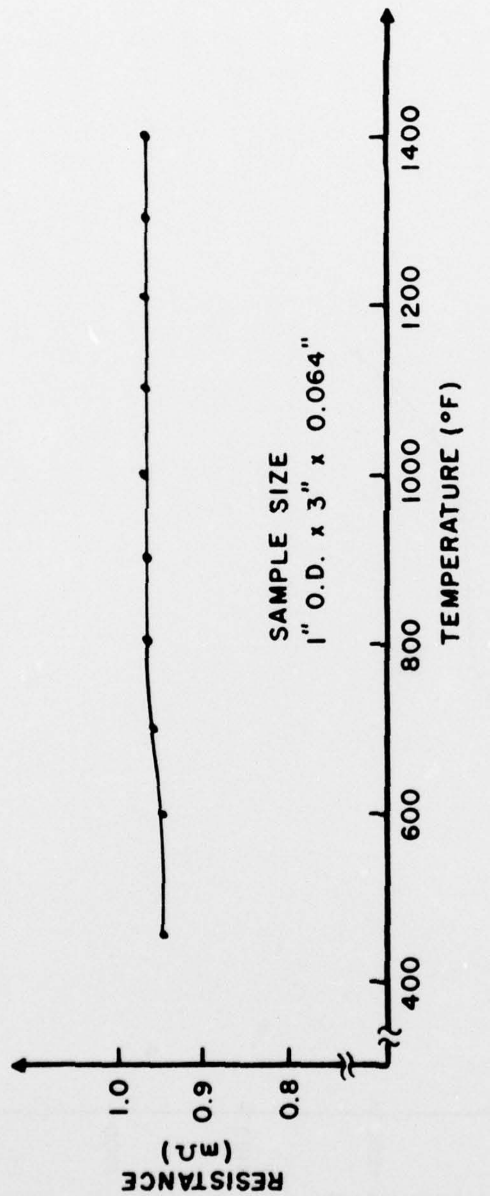

Figure 6. Resistance of Inconel 617 vs. Temperature

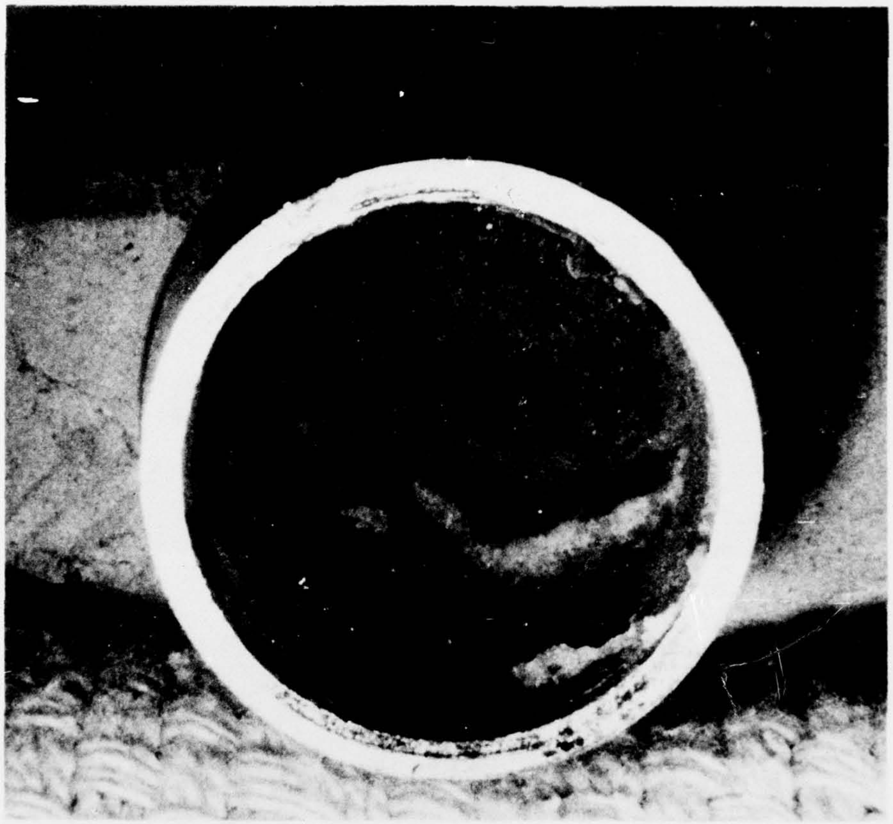

Figure 7. End View of Post-Test D.H.C. End Cap

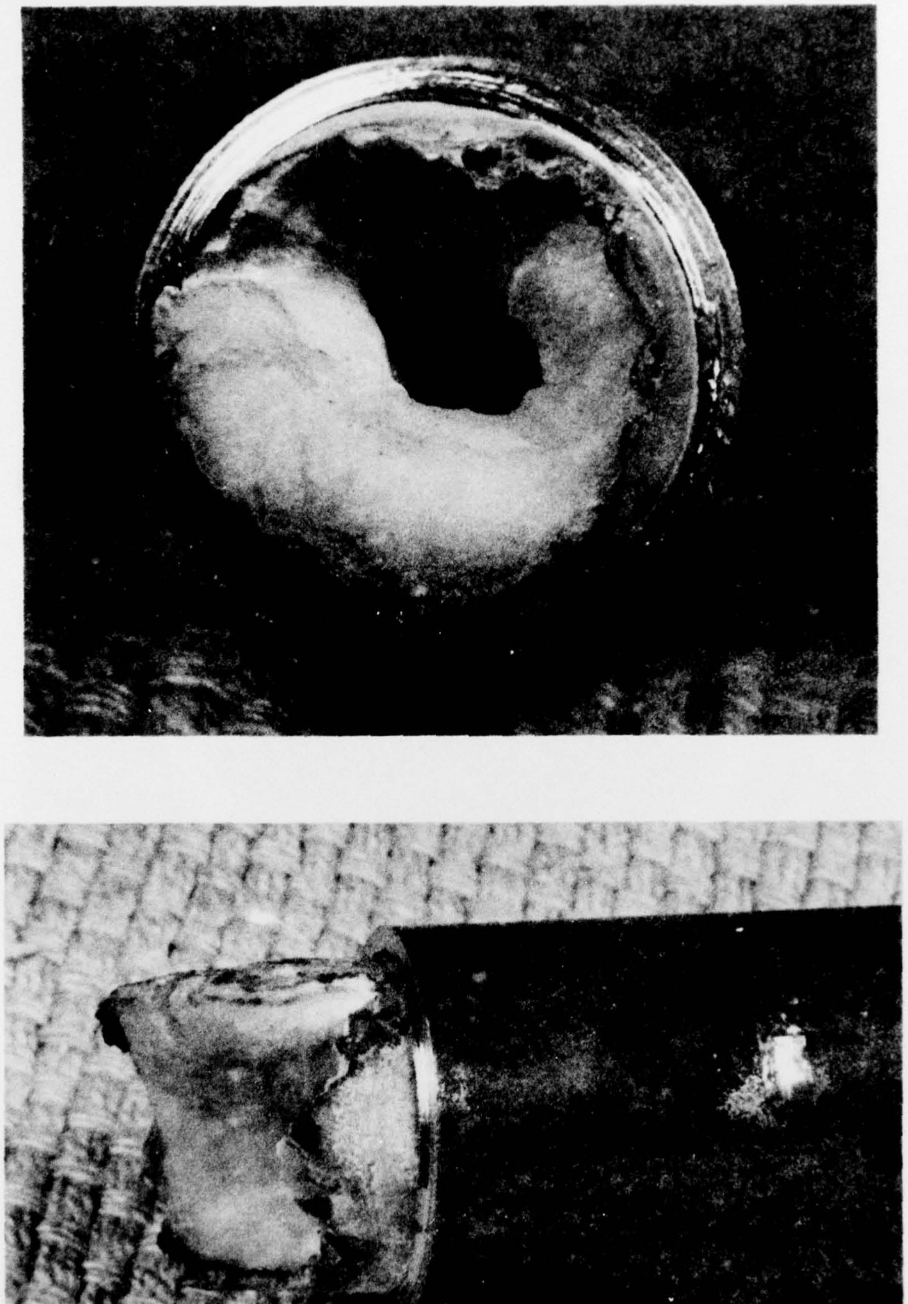

Figure 8. Views of Post-Test D.H.C. Salt

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